<u>Hazardous Air Pollutants (HAPS)</u>

<u>Of Interest for Fossil Fuel Fired Boilers</u>

Boiler Work Group

Of The

Industrial Combustion Coordinated Rulemaking (ICCR)

Federal Advisory Committee

September 4, 1998

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EXECUTIVE SUMMARY

This is the Boiler Work Group (BWG) report for the list of Hazardous Air Pollutants (HAPs) of Interest for fossil fired fuels (gas, distillate oil, residual oil and coal). It represents the consensus opinion of the Boiler Workgroup as determined in a meeting held in Ft. Collins, Colorado on April 30, 1998.

The BWG determined that the list of HAPs of Concern really be divided into three lists:

- HAPs OF INTEREST for further investigation
- HAPs that fall out on the HAPs of Interest List will then be looked at to see if they need to be tested. Those to be tested will become HAPs FOR FURTHER TESTING.
- HAPs FOR POTENTIAL REGULATION – These are HAPs that may need to be regulated or controlled.

A general protocol was developed to decide the final list of HAPs of Interest in each boiler fossil fuel group (natural gas, oils, and coal). The protocol included:

- Reviewing different reference sources to develop a list of HAPs of initial concern for each fuel category
- Compiling known emission rate data from reliable sources for those HAPs of initial concern,
- Determining the magnitude of HAPs emissions vented from boilers of 10 million BTU/hr (MMBTU/HR.), 100 MM BTU/HR., and 250 MM BTU/HR. firing rates.
- Comparing the actual emissions with deminimis limits derived from a very conservative stack model provided by the New Hampshire Dept. of Environmental Services (Air Resources Division).
- Performing a second screening of HAP of initial concern emission rates for a 250 MM BTU/Hr boiler. Actual emissions impact was determined using more realistic assumptions for the model boiler. The 250 MM BTU/Hr. boiler emissions were compared to the second round NHDES model levels, the Florida Ambient reference concentrations, and the BIF Levels (RAC).
- Developing the final list of HAPs of Interest for fossil fuel fired boilers based on:
    - HAPs that exceeded the models' screening levels
    - HAPs that were considered high toxic risks
    - HAPs that did not have enough data to support a recommendation

Below is the final List of HAPs of Interest. The HAPs that appear on this list may or may not appear on the list of HAPs for Testing or the list of HAPs for Regulation.

Table I. Gas HAPs of Interest List

Chemical	**Chemical**
Benzene	Phosphorus
Toluene	Dioxin
Hexane	Cadmium Compounds
POM's	Chromium Compounds
Formaldehyde	Cobalt Compounds
Nickel	Lead Compounds
Acetaldehyde	Manganese compounds
Dibenzofurans	

Table 2. Distillate Oil HAPs of Interest List

Chemical	**Chemical**
Benzene	Arsenic
1,3 Butadiene	Beryllium
Dioxins/Furans	Cadmium
POM's/Naphthalene	Chromium
Hydrochloric Acid	Lead
Hydrogen Fluoride	Manganese
Formaldehyde	Mercury
Acetaldehyde	Nickel

Table 3. Residual Oil HAPs of Interest List

Chemical	**Chemical**
Benzene	Arsenic
1,3 Butadiene	Beryllium
Dioxins/Furans	Cadmium
POM's/Naphthalene	Chromium
Hydrochloric Acid	Lead
Hydrogen Fluoride	Manganese
Formaldehyde	Mercury
Selenium	Nickel
	Phosphorus

Table 4. Coal HAPs of Interest List

Chemical	**Chemical**
Benzene	
Isophorone	Nickel
Dioxins	Phenol
POMs	Selenium
Hydrochloric Acid	Cyanide
Hydrogen Fluoride	Acrylamide
Acetaldehyde	Acrylonitrile
Acrolein	2-chloro-acetophone
Methyl Iodide	Ethylene Dibromide
Arsenic	Formaldehyde
Beryllium	Hexachlorobenzene
Cadmium	Methyl Chloride
Chromium	N-Nitrosodimethylamine
Lead	1,1,2,2 Tetrachloroethane
Phosphorus	Antimony Compounds
Manganese	Radionuclides
Mercury	Cobalt

II Introduction

The Boiler Work Group (BWG) of the Industrial Combustion Coordinated Rulemaking (ICCR) FACA process undertook the task of determining which Hazardous Air Pollutants (HAPs) of Interest should be listed for further study. The BWG further subdivided its group in to three subgroups: Fossil fired systems (oil, gas, and coal), clean wood fired systems, and non-fossil fired systems that included all the remaining boilers. This report will address the HAPs of Interest for fossil fired boilers (gas, oils and coal).

Major contributors to this consensus report are from the ad hoc HAPs subgroup members listed below:

NAME	REPRESENTING	ISSUE
Andrew Bodnarik	New Hampshire DES Air Resources	HAPs Review
Wendell Brough	Celanese	Natural Gas
Mark Bryson	Alcoa	Coal
Alex Johnson	Citizens Commission for Clean Air In the Lake Michigan Basin	Coal
Gunseli Shareef	Radian	Oil

The items included in this report reflect a consensus agreement among BWG members. Any dissenting comments will be so noted.

III. Definitions

The following topics were defined as a necessity to reach the final list of HAPs of Interest:

A. HAPs

1. HAPs of Interest

The HAPs list will be broken down into three distinct categories: HAPs of Interest, HAPs for Testing and HAPs for Regulation. The HAPs of interest included those chemicals that needed to be further investigated because they fell into one or more of the categories below:

- above initial screening levels and/or,
- potential of extreme toxicity
- listed as an urban air toxic

- HAPs having little or no emission data.

2. HAPs for Further Testing

HAPs that appear on the HAPs of Interest List will then be reviewed to see if they need to be tested. Those that don't have adequate emission data should be further tested. This list will become HAPs FOR FURTHER TESTING.

3. HAPs for Potential Regulation

These are HAPs of Interest that may need to be regulated or controlled. This list of HAPs of Potential Regulation may be longer or shorter than the list of HAPs of Interest or HAPs for Further Testing.

B. Natural Gas

The definition for Natural Gas was taken from the NSPS Rules in 40 CFR 60.41 b: a naturally occurring mixture of hydrocarbon and non-hydrocarbon gases found in geologic formations beneath the earth's surface, of which the principal constituent is methane; or (2) liquid petroleum gas, as defined by the American Society for Testing and Materials in ASTM D1835-82, "Standard Specification for Liquid Petroleum Gases".

For all practical purposes, this included wellhead gas (gas straight from the ground). Mercury in wellhead gas was initially a concern of the Boiler Work Group. However, a paper is provided as Appendix 1 discussing why Mercury should not be an issue.

Liquid Petroleum Gas (LPG): LPG is propane and/or butane often with small amounts of propylene and butylene sold as a pressurized liquid. LPG is included in this definition of Natural Gas.

<u>Gaseous Fuels Derived from processing of crude oil, petroleum or petrochemicals: There was not a consensus in the Boiler Work Group to include this in the definition of Natural Gas.</u> The Petroleum Environmental Research Forum Project 92-19 (PERF Data) found no significant difference in air toxic emissions between burning natural gas, as defined above, and these process derived gaseous fuels. Enclosed in Appendix 2, there is a paper entitled "Rationale for Broad Definition of Gaseous Fuels" which supports the argument of incorporating gaseous fuels derived from processing of crude oil, petroleum or petrochemicals into the definition of Natural Gas.

However, at this time, because of not being able to review and digest the information, the BWG did not come to consensus on this definition and is deferring to the EPA the decision of the incorporation of these process derived fuel types with Natural Gas.

C. Oils

- Distillate Oil (also called unheated oil): Fuel oils that comply with the specifications for fuel oil numbers 1 and 2, as defined by the American Society of Testing and Material in ASTM D396-78, Standard Specifications for Fuel Oil. (40 CFR 60.41 b)

- Residual Oil (also called heated oil): Crude oil, and all fuel oil numbers 4,5, and 6 as defined by the American Society of Testing and Materials in ASTM D-396-78, Standard Specifications for Fuel Oils. (40 CFR 60.41 b)

D. Coal

The coal definition is the same as that from 40 CFR 60.41b (NSPS Subpart Db) – Coal means all solid fuels classified as anthracite, bituminous, sub-bituminous, or lignite by the American Society of Testing and Materials in ASTM D388-77, Standard Specification for Classification of Coals by Rank, coal refuse, and petroleum coke. Coal-derived synthetic fuels, including but not limited to solvent refined coal, gasified coal, coal-oil mixtures are also included in this definition.

IV. Initial Selection Process

A. Initial Review of Data and Reference Material

For each type of fuel category for Fossil Fired Boilers (natural gas, distillate oil, residual oil, and coal) several reference sources were reviewed to determine an initial list of HAPs of Interest. These initial HAP references included: information from the Testing and Monitoring Protocol Work Group (TMPWG), data from API, data from WSPA, Dioxin presentation for the ICCR, AP-42, EPA Emissions Database, EPA MACT floor data presentation to the BWG, EPA Utility Boiler HAPs Study, Great Waters Program documents, EPA's proposed list of 40 priority HAPs for further analyses under the Urban Air Toxic Program, EPA's draft of Prioirty HAPs, and others. Specific references are listed in the document titled *Majority Report on Hazardous Air Pollutants (HAPs) of Concern, Boiler Work Group*, dated February 6, 1998 and in Attachment #2 of the Minority Report entitled *Additional Section 112 (b) and Section 129 Hazardous Air Pollutants of Concern for Industrial Boilers,* dated February 6, 1998. These reports were posted on the TTN by the EPA.

The EPA Utility Boiler HAPs Study can be used as an example of how a list of HAPs of Interest was developed by a particular resource. The EPA reviewed all of the emissions from large fossil fuel fired utility boilers. By modelling the actual emissions, the EPA looked at the health risks. They plugged the emission model information into health effects models to determine the inhalation and cancer risks. From this analysis, the EPA determined which HAPs should be further studied as HAPs of Interest in their Utility HAPs study.

When a HAP was found on multiple resource lists it was further investigated as a <u>HAP of Initial Concern</u>. HAPs not appearing on the various reference lists were not further investigated.

B. Compilation of Emission Data

To further investigate HAPs of Initial Concern various emission databases were reviewed. The emission database references include: EPA Utility Boiler HAPs Study, API/WSPA study, MACT Floor Presentations by the EPA based on the EPA Emissions database, the Fifth Edition of AP-42, EPA Emissions Database, and TMPWG information to mention a few. Again, the specific information can be found in the *Majority Report on Hazardous Air Pollutants (HAPs) of Concern, Boiler Work Group*, dated February 6, 1998 (*Majority HAPs Report)* and in Attachments1,2, and 3 of the report entitled *Additional Section 112 (b) and Section 129 Hazardous Air Pollutants of Concern for Industrial Boilers,* dated February 6, 1998 (

All of the emission review data is compiled into tables found in the *Majority HAPs Report*.

Comparisons were then run using the worst emissions or median values from multiple tests (coal) from the various data reference sources. These “worst case” actual emissions were used to determine the total emissions US-wide and to calculate emissions for a 10 million BTU/hour (MMBTU/hr.) boiler, a 100 MMBTU/hr. boiler and a 250 MMBTU/hr. boiler. These boiler sizes were picked because they represent the sizes of typical industrial boilers. These calculated boiler emissions were then used as a standard for comparison against a the screening models, as described below.

<u>V. Comparison of Emission Data to Deminimis Air Model – Initial Screening</u>

There was an initial screening performed by comparing the boiler emissions from a 250 MM BTU/hr. boiler with a New Hampshire Department of Environmental Services (NHDES) Deminimis Emission Model. The HAPs Subgroup believed that this conservative model comparison step was a necessary part of the HAPs determination process. From the Model a list of draft deminmis limits was determined by the NHDES. It was believed then, that any emissions that were lower than the NHDES proposed deminimis limits could automatically be dropped from the list of concerns.

This NHDES Screening Model used the following conservative assumptions in a US EPA air pollution dispersion model for a "typical facility with downwash problems":

- Emission rate = 1 lb/hr.
- Stack Height = 10 ft.
- Stack diameter = 1 ft.
- Volume flow = 100 ACFM
- Temperature = 68 degrees F
- Building height = 10 ft., width = 20 ft. and length = 20 ft.

This equates to a stack velocity of about 1 to 2 ft./sec. However, in industry, economic stack velocities usually start at about 10 ft/sec. and can go as high as 100 ft/sec. Typical stack gas velocities are usually more than 20 ft/sec. The temperature in the model stack is only 68 degrees F. Most industrial boiler stack temperatures are at least 200 to 300 degrees F, even with efficient economizers. A temperature of 68 degrees will cause zero buoyancy of the exiting gas. This type of model would proabably not allow drafting in a boiler.

Basically this model guarantees maximum downstream downwash of any constituents and will predict much higher concentrations of emitted species at the point of impact than would be found under more realistic conditions. Finally, the model deminimis limits were set based on the health effects concentrations that the downstream receptors would encounter. Then the conservative emission rates were backcalculated. All of this is discussed to show the conservativeness of the model and the belief that if the actual emissions for a 250 MM BTU/HR. boiler were less than the the deminimis emissions then the HAP would be at low risk for posing any health problem.

Therefore, any HAP whose emissions were below the deminimis levels from the deminimis model were initially considered for dropping from the list HAPs of initial concern.

The emission comparisons are found in the *Majority HAPs Report*.

VI. Secondary Comparison Considerations

As stated above the NHDES model is an extremely conservative air emission model. This initial model was revised to us more realistic boiler stack parameters and US EPA refined air pollution dispersion models. The boiler stack parameters were derived from an analysis of existing boilers burning oil and wood permitted in New Hampshire. The new stack parameters are shown in a memo from the NHDES dated March 23, 1998 located in Appendix 3. It should be noted that the model used for the comparison was a dispersion model set up for wood firing conditions. At the time of this screening gas and coal model data were not available. However, in most cases actual boiler groundlevel concentrations used for the comparison were several orders of magnitude below the NHDES second screen wood model emissions.

This comparison was then made with the remaining constituents on the <u>HAPs of Initial Concern</u> list. Those constituents whose emission rates from a 250 MM BTU/hr. boiler were below this second round screening were then dropped or discussed for dropping.

Then the final list of <u>HAPs of Interest</u> was determined. There were several constituents that may have been dropped from one or both screenings but were left on the List of Concern for one of the following reasons:

- Multiple boilers in an area may emit quantities of the HAP that may cause risk to the population,
- The HAP may appear on the proposed Urban Air Toxic list (112[k]) and is at an emission level that may cause some concern (example – Formaldehyde, dioxans/furans)
- The HAP may appear on a list of extreme toxicity (no definition of the limits) and is at an emission rate that may cause some concern. Additionally the HAP is purported to be a combustion by-product. (Examples- methylene chloride and 1,1,2,2 tetrachloroethane).
- The HAP had little or no emission data.

A set of tables showing each fossil fuel type is shown in Appendix 4. These tables show the rationale for leaving the HAP on the list of HAPs of Concern. It is a summary of the concepts shown above.

VII. Consensus HAPs of Interest List

After all of the above screening processes were performed consensus was made within the ad hoc HAPs subgroup and the BWG at the meeting on April 29, 1998. Below is a list of the HAPs of Interest for each of the fossil fuel groups (gas, distillate oil, residual oil and coal).

Table I. Gas HAPs of Interest List

Chemical	Chemical
Benzene	Phosphorus
Toluene	Dioxin
Hexane	Cadmium Compounds
POM's	Chromium Compounds
Formaldehyde	Cobalt Compounds
Nickel	Lead Compounds
Acetaldehyde	Manganese compounds
Dibenzofurans	

Table 2. Distillate Oil HAPs of Interest List

Chemical	Chemical
Benzene	Arsenic
1,3 Butadiene	Beryllium
Dioxins/Furans	Cadmium
POM's/Naphthalene	Chromium
Hydrochloric Acid	Lead
Hydrogen Fluoride	Manganese
Formaldehyde	Mercury
Acetaldehyde	Nickel

Table 3. Residual Oil HAPs of Interest List

Chemical	**Chemical**
Benzene	Arsenic
1,3 Butadiene	Beryllium
Dioxins/Furans	Cadmium
POM's/Naphthalene	Chromium
Hydrochloric Acid	Lead
Hydrogen Fluoride	Manganese
Formaldehyde	Mercury
Selenium	Nickel
	Phosphorus

Table 4. Coal HAPs of Interest List

Chemical	**Chemical**
Benzene	
Isophorone	Nickel
Dioxins	Phenol
POMs	Selenium
Hydrochloric Acid	Cyanide
Hydrogen Fluoride	Acrylamide
Acetaldehyde	Acrylonitrile
Acrolein	2-chloro-acetophone
Arsenic	Ethylene Dibromide
Beryllium	Formaldehyde
Cadmium	Hexachlorobenzene
Chromium	Methyl Chloride
Cobalt	Methyl Iodide
Lead	N-Nitrosodimethylamine
Phosphorus	1,1,2,2 Tetrachloroethane
Manganese	Antimony Compounds
Mercury	Radionuclides

Appendix 1

MERCURY IN WELLHEAD GAS

6/9/98-draft

MERCURY IN WELLHEAD GAS

Finding – Mercury emissions from wellhead gas combustion are insignificant nationwide, and even in those remote geographical areas with the highest mercury concentrations, emissions are about two pounds a year or less.

Wellhead Gas

"Wellhead"[5] gas is natural gas produced directly from underground reservoirs without having removed the natural gas liquids (butane, propane, gasoline, etc.). The Btu content of this gas can range as high as 1200 Btu as compared to approximately 1000 Btu for natural gas being transported to market via Department of Transportation (DOT) regulated pipelines.

"Natural gas", as discussed in this Section III B of this document, is pipeline quality gas located downstream of the natural gas plant. Wellhead gas is processed and the natural gas liquids are removed to produce marketable natural gas. Testing by the Gas Research Institute (GRI) of natural gas demonstrates it has only a trace mercury concentration as noted in GRI's Report[3]. The maximum mercury concentration found in natural gas was 0.2 micrograms per cubic meter (ug/m^3).

Wellhead gas is only used as fuel in oil and gas industry operations where processed gas cannot be obtained from a natural gas plant. This lack of processed gas could be due to the absence of a DOT regulated pipeline to market or the remaining gas in the producing field is depleted to such an extent that the gas plant has been shut down due to economic considerations. Wellhead gas can be used in boilers, heater treaters, or IC engines at isolated oil and gas field locations.

Boilers are rarely used at oil and gas facilities outside of California. Boilers are used in California for generating steam for injection into high viscous oil reservoirs for recovery purposes. Nearly all of the boilers in California use natural gas with a few using wellhead gas. Mercury is not found in California wellhead gas above trace quantities (1-100 ug/m^3).

Heater treaters and IC engines use wellhead gas at certain oil and gas facilities nationwide.. The only know geographical area with mercury greater than 100 ug/m^3 is in South Texas (2-3 County Area)[4].

Mercury in Wellhead Gas

Elemental mercury[1] was found in wellhead gas as early as 1969 in Holland. In addition, mercury corrosion was detected in an aluminum spiral wound heat exchanger at a liquid natural gas plant in Skikda, Algeria in 1974. Since this time, mercury in wellhead gas has become a major concern in cryogenic gas processing industries. These industries often use aluminum heat exchangers in their processes. Mercury corrosion of aluminum exchangers has led to several equipment failures since the problems at Skikda.

Mercury forms[1] are present in some wellhead gas and wellhead gas associated condensates, as organometallic and inorganic compounds, and in the elemental (metallic) form depending on the origin of the gas. The elemental form can be found in either the vapor or liquid phase. The organometallic and inorganic compounds drop into the liquid phase in any fractionation of the natural gas streams. Vapor phase elemental mercury is a primary culprit in corrosion of aluminum exchangers inside cryogenic cold boxes. Operators typically remove mercury upstream of the natural gas plant to prevent corrosion of aluminum equipment within the plant as well as prevent corrosion at facilities downstream of the plant. Mercury is not removed from wellhead gas combusted at production sites.

Mercury has been found in wellhead gas at a few geographic locations nationwide. Mercury concentrations range from 0.02 – .40 micrograms per cubic meter in the Gulf Coast Area[2]; 5 – 15 micrograms per cubic meter in the Overthrust Belt/Kansas[2,4]; and as high as 500 micrograms per cubic meter in some South Texas fields[4]. Gas plant operators test for mercury because cryogenic fractionation processes can be damaged by mercury concentrations as low as 1-10 micrograms per cubic meter. Operators utilize different processes worldwide to remove mercury from the plant inlet gas stream to protect sensitive components from corrosion. Again, the mercury removal systems are intended to protect the process equipment in the gas processing plant; they have nothing to do with improving combustion. In fact, most cryogenic plant operators do not find it necessary to remove trace mercury concentrations from wellhead gas to prevent corrosion.

Wellhead Gas as Fuel

For the purposes of Combustion MACT, there are three main reasons why mercury in wellhead gas is not significant.:

1. Wellhead gas is nearly always used in oil and gas operations upstream of the natural gas plant. The typical type of equipment used in these operations is small and widely separated geographically. Nearly all heaters are smaller than 3 MMBTU/Hr. and most internal combustion engines are less than 1000

horsepower in size. Most of these production facilities will not have more than one of these emission sources per site.

2. Concentrations of mercury in produced wellhead gas are very low in the United States. Mercury concentrations range from 0.02 micrograms per cubic meter to 500 micrograms per cubic meter. Consequently, annual emissions of mercury from typical oil and gas production equipment are very low as calculated[6] in the following tables:

Gulf of Mexico (0.4 ug/m^3 mercury in wellhead gas)

Equipment Size	Pounds/Yr.	Tons/Yr.
3 Million BTU Heater	0.00066	3.31×10^{-7}
1000 HP IC Engine	0.00187	9.36×10^{-7}

Overthurst Belt/Kansas (15 ug/m^3 mercury in wellhead gas)

Equipment Size	Pounds/Yr.	Tons/Yr.
3 Million BTU Heater	0.025	1.26×10^{-5}
1000 HP IC Engine	0.070	3.51×10^{-5}

South Texas (500 ug/m^3 mercury in wellhead gas)

Equipment BTU Heater	Pounds/Yr.	Tons/Yr.
3 Million BTU Heater	0.820	4.10×10^{-4}
1000 HP IC Engine	2.320	1.16×10^{-3}

Note: These emission calculations assume that the total mercury in the fuel gas is emitted to the atmosphere after combustion; leading to a potential overestimate. In addition, the mercury estimates may be high because they are based on pure methane combustion which has a lower Btu value resulting in a higher fuel throughput.

3. Wellhead gas containing more than trace concentrations of mercury is only found in South Texas. In this geographical area, oil and gas production facilities are generally located in arid and rural areas.

REFERENCES

1. Rios, Julio A., Coyle, David A., Durr, Charles A. and Frankie, Brian M. “Removal of Trace Mercury Contaminants from Gas and Liquid Streams in the LNG and Gas Processing Industry”, 77th Annual Convention, Gas Producers Association, March 16-18, 1998.
2. “GRI Mercury Removal Technology (Hgone) Process Design and Engineering”, Vol.1, Gas Research Institute Report 96/0018.1, 1995.
3. “Characterization and Measurement of Natural Gas Trace Constituents Volume II: Natural Gas Survey”, Gas Research Institute 94/0243.2, 1995.
4. Lewis, Larry L., “Measurement of Mercury in Natural Gas Streams” in the 77th Annual Convention, Gas Producers Association, 1995.
5. “Field Handling of Natural Gas”, Third Edition, Natural Gas Processors Association, 1972.
6. McCarthy, James, “Interoffice Memo to Bob Welch, Columbia Gas, and Bill Freeman, Shell – ICCR Question on Mercury in Unprocessed Gas”, March 7, 1998.

Appendix 2: Boilers Working Group - MACT Floor Documentation

Rationale for Broad Definition of Gaseous Fuels

Boilers Working Group - MACT Floor Documentation

Rationale for Broad Definition of Gaseous Fuels

Background

Emissions data on HAPs and criteria pollutants used in the MACT determination process originated from several sources, and have gone through several stages of screening and assessment, as described in the Boilers Working Group “HAPs of Interest Analysis”. For gas-fired external combustion devices (i.e. Boilers and Process Heaters) three primary sources were utilized.

First, source test results collected under the California Air Toxics "Hot Spots" Inventory and Assessment Act (AB2588) have been compiled and quality reviewed in a joint effort by the Western States Petroleum Association (WSPA), the California Air Resources Board (CARB), and the American Petroleum Institute (API). The results of this investigation are compiled in the 3-volume Draft Report titled "Development of Toxics Emission Factors for Petroleum Industrial Combustion Sources" (D. W. Hansell and G. C. England, EER Corporation, September 1997). It was provided to the US EPA in October 1997, and is available in the ICCR docket. A presentation on this database was provided to a joint meeting of all the ICCR Work Group members on November 18, 1997. The validation and verification processes used to quality assure these data makes this the most reliable and comprehensive compilation of field emission source test data for petroleum industry combustion sources. The final report is currently being printed by API (August 1998) and will be available to the Coordinating Committee and the US EPA by mid-September.

The second source of emissions test data came from the Petroleum Environmental Research Forum (PERF) 92-19 "Toxic Combustion Byproducts" project. In 1992 PERF initiated a Cooperative Research and Development Agreement (CRADA) with the U.S. Department of Energy, and with EPA participation, performed an experimental and fundamental investigation of chemical and physical mechanisms governing organic HAP formation, destruction, and emissions. These tests on full-scale burners were performed at the Sandia National Laboratories/Livermore. This program produced data of very high quality that shed light on many of the key questions surrounding the field data. The results of this project were presented to the Coordinating Committee on July 22, 1997, and are summarized in a paper titled "Organic Hazardous Air Pollutant Emissions from Gas-Fired Boilers and Process Heaters" (G.C. England and D.W.Hansell, EER Corporation, July 1997) which is available in the ICCR docket. The PERF 92-19 CRADA Final Report, "The Origin and Fate of Toxic Combustion Byproducts in Refinery Heaters: Research to Enable Efficient Compliance with the Clean Air Act" (August 5, 1997), and be accessed at http://www.epa.gov/ttn/iccr/dirss/perfrept.pdf. The complete 10-volume study including test reports and appendices has been placed in the ICCR docket.

Lastly, the ICCR Emissions Database, V.2, provides a compilation of emissions test data made available from existing electronic databases such as STIRS, and other information from state and local agencies. Emissions information collected from the 114 ICR survey was also added to this database.

Conclusions

Based on the discussion above and the references cited therein, we conclude that:

- ***HAP emissions from all gas-fired sources are generally very low, but exhibit inherent variability associated with process fluctuations and sampling and analysis uncertainties*.**

  The PERF data referenced above demonstrate that HAP emissions from typical industry gas fired burners, under a variety of operating conditions are all very low, at or near the detection limits of the best measurement methods. In addition, field source test data, such as the WSPA/API database indicate that annual total HAP emissions from operating gas-fired heaters and boilers are well below the major source definition.

- ***HAP emissions from devices fired by either natural gas or petroleum processing derived gas are similar, on a Btu basis.***

  The controlled laboratory testing (PERF study) and the WSPA/API field test data demonstrate that emissions factors derived independently for different gaseous fuels are indistinguishable, when measurement uncertainty and process variability are taken into account (Figures 1). The emission factor derivation process accounts for the different heat content of the variety of the gases used in practice, and which like natural gas, consist primarily of hydrocarbons mixtures.

- ***HAP emissions from gas-fired boilers and process heaters are equivalent*.**

  Design practices are such that the same burner types are used for constructing both gas-fired process heaters and boilers. In addition, the field emissions data for boilers and process heaters, fired by a variety of gaseous and liquid fuels, was shown to be similar (Figure 2). The data demonstrate that emissions from boilers or process heaters vary by size (heat input) but are otherwise expected to be equivalent.

Recommendations

For the purposes of subcategorizing boilers – it is recommended that a single subcategory be established for devices firing the following gaseous fuels:

1. *Natural Gas/Wellhead Gas:* a naturally occurring mixture of hydrocarbon and non-hydrocarbon gases found in geologic formations beneath the earth's surface, of which the principal constituent is methane;
2. *Liquid Petroleum Gas:* as defined by the American Society of Testing and Materials in ASTM D1835-82, Standard Specification for Liquid Petroleum gases.
3. *Petroleum Derived Gas:* Gaseous fuel derived from the processing of crude oil, petroleum, or petrochemicals.

Since consistent definitions of the fuels combusted are desirable for all ICCR sources, we recommend that the Coordinating Committee adopt the three-part definition above which is consistent with that adopted by both the Process Heaters and Turbines Working Groups for their gaseous fired devices.

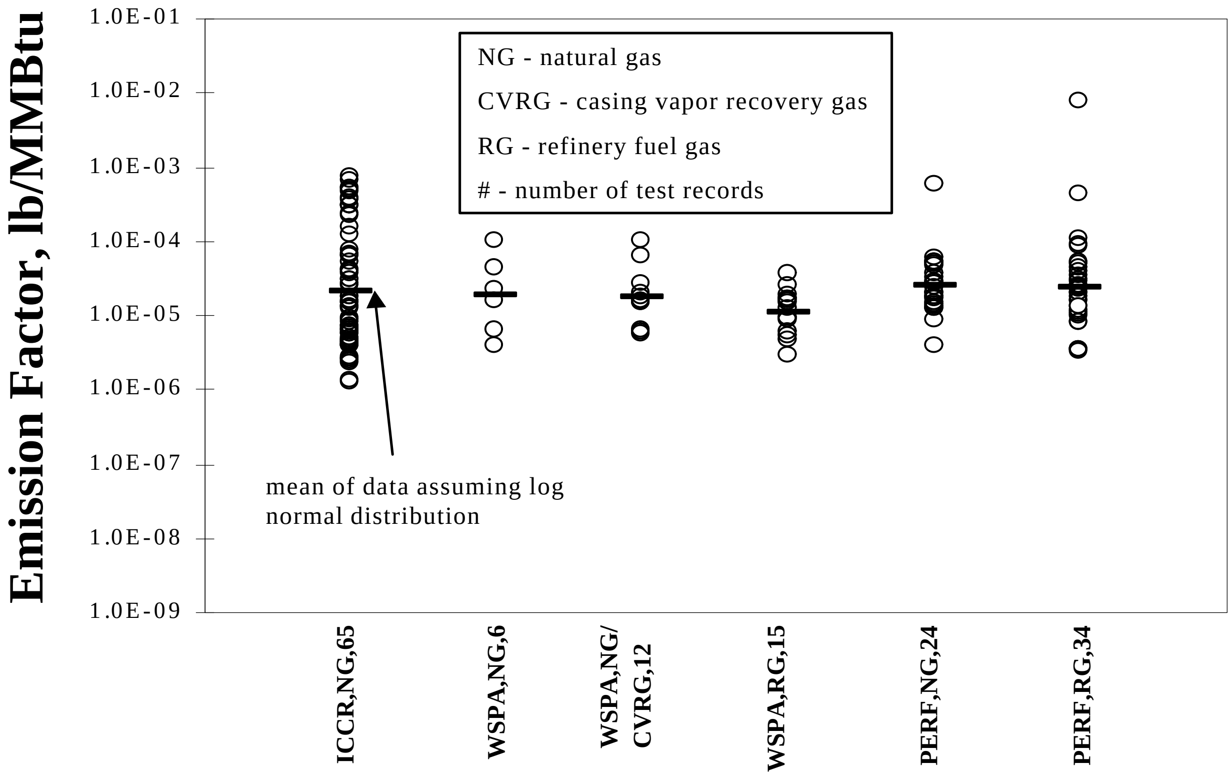
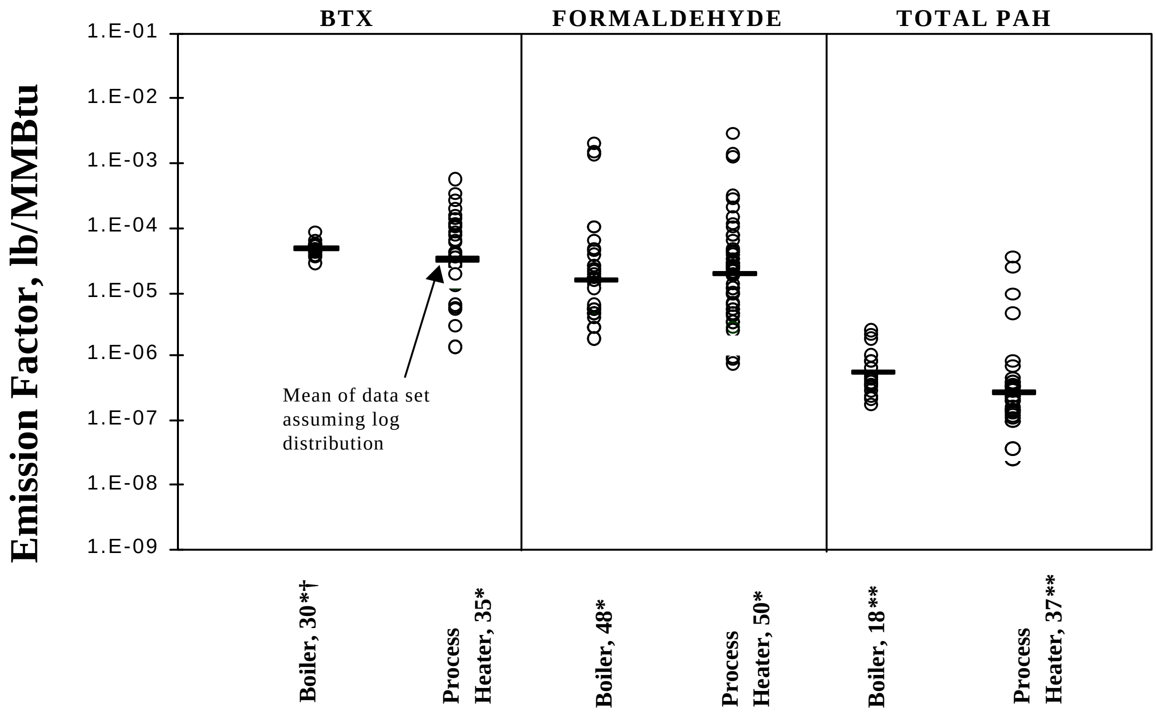


Figure 1. Formaldehyde emissions as a function of fuel type for gas fuel fired boilers (ICCR, WSPA, and PERF data).



* Includes crude, FO #6, and gaseous fuel (primarily gas)

** Includes FO #6 and gaseous fuel (primarily gas)

† Number following label = number of test records

Figure 2. Comparison of HAP emissions data for Boilers and Process Heaters (WSPA data).

Appendix 3

ICCR Modeling for Hypothetical Oil and Wood Boilers

From the

New Hampshire Dept. of Environmental Services

STATE OF NEW HAMPSHIRE
IntraOffice Memorandum

Department of Environmental Services
Air Resources Division

TO: Andy Bodnarik, Administrator DATE: March 23, 1998
Engineering Bureau

FROM: Jim Black, Modeling Supervisor
Technical Services Bureau

SUBJ: ICCR Modeling for Hypothetical Oil and Wood Boilers

Based on our discussions of March 18 regarding the modeling of hypothetical oil and wood fired boilers, I have completed a set of screening and refined modeling runs. Runs were made for flat, complex and simple terrain, assuming relatively hilly terrain in the latter two cases. Both annual and 24-hour average concentrations were calculated. The following inputs were used:

Parameter	Oil Condition	Wood Condition
Stack Height	200 ft	180 ft
Stack Diameter	9 ft	7.5 ft
Volume Flow	150,000 ACFM	125,000 ACFM
Gas Temperature	350^{o} F	330^{o} F
Emission Rate	1 lb/hr	1 lb/hr
Building Height	90 ft	90 ft
Building Width	80 ft	80 ft
Building Length	80 ft	80 ft

The above inputs were derived from a study of large boilers burning both oil and wood which have been permitted in this state. The building data are representative of a typical boiler building for facilities which have previously been modeled. Using this size building, small but measurable downwash effects were predicted.

For the simple terrain modeling, gradually rising terrain was assumed in all directions, typical of a valley situation with surrounding rising hills. Elevations were assumed to reach stack top just beyond one kilometer and plume height close to three kilometers. This is conservative, though not unrealistic, topography and, in conjunction with the flat terrain modeling, presents a full range of terrain conditions.

Using the above input data, the following maximum impacts were predicted:

Maximum 24-Hour Average Concentrations

	Oil Condition			Wood Condition		
Terrain	**Flat**	**Simple**	**Complex**	**Flat**	**Simple**	**Complex**
Screening Impact (ug/m^3)	0.13	**0.47**	0.23	0.21	**0.68**	0.31
Distance (m)	990	1200 (a)	3000 (b)	270	1100 (a)	2500 (b)
Refined Impact (ug/m^3)	0.12	**0.30**	(c)	0.18	**0.42**	(c)
Distance (m)	300	300		300	1000	

Maximum Annual Average Concentrations

	Oil Condition			Wood Condition		
Terrain	**Flat**	**Simple**	**Complex**	**Flat**	**Simple**	**Complex**
Screening Impact (ug/m^3)	0.033	**0.118**	0.058	0.053	**0.170**	0.078
Distance (m)	990	1200 (a)	3000 (b)	270	1100 (a)	2500 (b)
Refined Impact (ug/m^3)	0.008	**0.029**	(c)	0.017	**0.047**	(c)
Distance (m)	300	2000		300	1000	

Notes: (a) stack top height was assumed to be reached at this distance
(b) plume height was assumed to be reached at this distance
(c) modeled in conjunction with simple terrain (maximum impacts)

Please contact me if you have any questions regarding the results.

c:C.Beahm

Appendix 4.

Rationale for Selection of Fossil Fuel HAPs

Table A – Gas HAPs of Interest

Table B – Distillate Oil HAPs of Interest

Table C – Residual Oil HAPs of Interest

Table D – Coal HAPs of Interest

	Table A:	Selection Rationale - Gas HAPs of Interest							
9/3/98									
Classification	**Component**	> NHDES Deminimis(1)	> NHDES Indust. Model (2)	Urban Air Toxics List (3)	Great Lakes Strategy/Great Waters (4)	Health Risk in Detroit (5)	Highly Toxic HAP (6)	Not Enough Data	Other
Volitiles	Benzene	X		X		X			
	Toluene								O3 Precursor
	Hexane	X	Not Modeled					X	
Semi Volatiles	POMs			X	X	X	X		
Carbonyls	Acetaldehyde			X					
	Formaldehyde	X		X		X			
Metals	Cadmium	X		X		X	X		
	Chromium	X		X		X	X		
	Cobalt	X			X				
	Lead	X		X	X	X	X		
	Manganese	X		X	X	X	X		
	Nickel	X		X	X	X	X		
Other	Dibenzofurans	ND	N/A	X	X	X	X	X	
	Dioxins	ND	N/A	X	X	X	X	X	
	Phosphorus	X	Not Modeled						

(1) Comparison with conservative NHDES Model (250 MM BTU/Hr. boiler Comparison)
(2) Comparison with industrial NHDES Model (250 MM BTU/Hr. boiler Comparison). Only model data comparison available was for wood boiler emissions.
(3) Hazardous Air Pollutant Area Source Program (CAA Subsect. 112(k) - Urban Air Toxics Study Priority HAP List of 40
(4) Listed on one or more of the following Great Lakes Area Programs:
- Great Waters Progam, CAA Subsect. 112(m)
- Great Lakes Binational Toxics Strategy, International Joint Commission *Focu,* Vol. 22, Issue 2, 1997
- Critial Pollutant from EPA Revised Draft of Lake Michigan Lakewide Management Plan For Tox. Pollutants, 8/30/93
- Great Lakes Commissions, Great Lakes Regional Air Toxics Emissions Inventory of 49 Targeted Compounds

(5) Health Risk in Detroit - Ref. The Transboundary Air Toxics Study, EPA Final Summary Report, Dec. 1990
(6) Highly Toxic HAP's (Potency), Ref. EPA's Draft of Priority HAP's (5/13/97)

N/D - Not enough Data
N/A - Not Applicable

	Table B:	**Selection Rationale - Distillate Oil HAPs of Interest**							
8/25/98	9/3/98								
Classification	**Component**	> NHDES Deminimis(1)	> NHDES Indust. Model (2)	Urban Air Toxics List (3)	Great Lakes Strategy/Great Waters (4)	Health Risk in Detroit (5)	Highly Toxic HAP (6)	Not Enough Data	Other
Volatiles	Benzene	X(1a)	(1a)	X		X			
	1,3 Butadiene	1(a)	Not Modeled	X					
Semi Volatiles	Dioxins/Furans	ND	N/A	X	X	X	X	X	
	POMs/naphthalene	ND	N/A	X	X	X	X		
Acid Gases	Hydrochloric acid	ND						X	
	Hydrogen fluoride	ND	N/A					X	
Aldehydes/ketones	Formaldehyde			X		X			
	Acetaldehyde	1(A)		X				X	
Metals	Arsenic	X		X		X	X		
	Beryllium	X		X		X	X		
	Cadmium	X		X		X	X		
	Chromium	X		X		X	X		
	Lead	X		X	X	X	X		
	Manganese	X		X	X	X	X		
	Mercury	X		X	X	X	X		
	Nickel	X		X	X	X	X		

(1) Comparison with conservative NHDES Model (250 MM BTU/Hr. boiler Comparison)

(1a) Compound Values assumed the same as for Gas. According to PERF Analysis and Report.

(2) Comparison with industrial NHDES Model (250 MM BTU/Hr. boiler Comparison). Only model data comparison available was for wood boiler emissions.

(3) Hazardous Air Pollutant Area Source Program (CAA Subsect. 112(k) - Urban Air Toxics Study Priority HAP List of 40

(4) Listed on one or more of the following Great Lakes Area Programs:

Great Waters Progam, CAA Subsect. 112(m)

Great Lakes Binational Toxics Strategy, International Joint Commission, *Focus,* Vol. 22, Issue 2, 1997

Critial Pollutant from EPA Revised Draft of Lake Michigan Lakewide Management Plan For Tox. Pollutants, 8/30/93

Great Lakes Commissions, Great Lakes Regional Air Toxics Emissions Inventory of 49 Targeted Compounds

(5) Health Risk in Detroit - Ref. The Transboundary Air Toxics Study, EPA Final Summary Report, Dec. 1990

(6) Highly Toxic HAP's (Potency), Ref. EPA's Draft of Priority HAP's (5/13/97)

ND - Not enough Data

N/A - Not applicable

Table C: **Selection Rationale - Residual Oil HAPs of Interest**

9/3/98

Classification	**Component**	> NHDES Deminimis(1)	> NHDES Indust. Model (2)	Urban Air Toxics List (3)	Great Lakes Strategy/Great Waters (4)	Health Risk in Detroit (5)	Highly Toxic HAP (6)	Not Enough Data	Other
Volatiles	Benzene	X		X		X			
	1,3 Butadiene	ND	N/A	X				X	
Semi Volatiles	POMs/naphthalene	ND	N/A	X	X	X	X	X	
Acid Gases	Hydrochloric acid	X							
	Hydrogen fluoride	X							
Aldehydes/ketones	Formaldehyde	X		X		X			
Metals	Arsenic	X		X		X	X		
	Beryllium	X		X		X	X		
	Cadmium	X		X		X	X		
	Chromium	X		X		X	X		
	Lead	X		X	X	X	X		
	Manganese	X		X	X	X	X		
	Mercury	X		X	X	X	X		
	Nickel	X		X	X	X	X		
	Selenium	X				X			
	Phosphorus	X							
Other	Dioxins/Furans	ND	N/A	X	X	X	X	X	

(1) Comparison with conservative NHDES Model (250 MM BTU/Hr. boiler Comparison)

(2) Comparison with industrial NHDES Model (250 MM BTU/Hr. boiler Comparison). Only model data comparison available was for wood boiler emissions.

(3) Hazardous Air Pollutant Area Source Program (CAA Subsect. 112(k) - Urban Air Toxics Study Priority HAP List of 40

(4) Listed on one or more of the following Great Lakes Area Programs:

Great Waters Progam, CAA Subsect. 112(m)

Great Lakes Binational Toxics Strategy, International Joint Commission, *Focu,* Vol. 22, Issue 2, 1997

Critial Pollutant from EPA Revised Draft of Lake Michigan Lakewide Management Plan For Tox. Pollutants, 8/30/93

Great Lakes Commissions, Great Lakes Regional Air Toxics Emissions Inventory of 49 Targeted Compounds

(5) Health Risk in Detroit - Ref. The Transboundary Air Toxics Study, EPA Final Summary Report, Dec. 1990

(6) Highly Toxic HAP's (Potency), Ref. EPA's Draft of Priority HAP's (5/13/97)

ND - Not enough Data

N/A - Not Applicable

Table D:	Selection Rationale - Coal HAPs of Interest								
9/2/98									
				Urban Air	Great Lakes	Health Risk in	Highly Toxic	Not Enough	Other
		> NHDES	> NHDES Indust.	Toxics List (3)	Strategy/Great	Detroit (5)	HAP (6)	Data	
CAS	***Chemical***	Deminimis	Model		Waters (4)				
Number	***Name***								
75070	Acetaldehyde			X					
107028	Acrolein			X			X		
79061	Acrylamide	X	Not Modeled	X		X	X		
107131	Acrylonitrile	X		X		X	X		
71432	Benzene	X		X		X			
2142689	2-chloro acetophenone	X	Not Modeled						
106934	Ethylene dibromide (Dibromoethane)			X		X	X		
50000	Formaldehyde	X		X		X			
118741	Hexachlorobenzene	X	Not Modeled		X		X		
7647010	Hydrochloric acid	X	Not Modeled						
7664393	Hydrogen fluoride (Hydrofluoric acid)	X	Not Modeled						
78591	Isophorone								
74873	Methyl chloride (Chloromethane)			X		X			
74884	Methyl Iodide	ND	N/A					X	
62759	N-Nitrosodimethylamine	X	Not Modeled						
108952	Phenol				X				
7723140	Phosphorus	X	Not Modeled						
79345	1,1,2,2-Tetrachloroethane			X					
0	Antimony Compounds	X							
0	Arsenic Compounds	X		X		X	X		
0	Beryllium Compounds	X		X		X	X		
0	Cadmium Compounds	X		X		X	X		
0	Chromium Compounds	X		X		X	X		
0	Cobalt Compounds	X			X				
0	Cyanide Compounds1	X	Not Modeled						
0	Lead Compounds	X		X	X	X	X		
0	Manganese Compounds	X		X	X	X	X		
0	Mercury Compounds	X		X	X	X	X		
0	Nickel Compounds	X		X	X	X	X		
0	Polycylic Organic Matter (POM)	ND	N/A	X	X	X	X	X	
0	Radionuclides	X	Not Modeled						On EPA Utility Coal HAPs for further Study
0	Selenium Compounds	X				X			
	Dioxins	ND	N/A	X	X	X	X	X	

(1) Comparison with conservative NHDES Model (250 MM BTU/Hr. boiler Comparison)

(2) Comparison with industrial NHDES Model (250 MM BTU/Hr. boiler Comparison). Only model data comparison available was for wood boiler emissions.

(3) Hazardous Air Pollutant Area Source Program (CAA Subsect. 112(k) - Urban Air Toxics Study Priority HAP List of 40

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(5) Health Risk in Detroit - Ref. The Transboundary Air Toxics Study, EPA Final Summary Report, Dec. 1990

(6) Highly Toxic HAP's (Potency), Ref. EPA's Draft of Priority HAP's (5/13/97)

ND - Not enough data in emission database.

N/A - Not Applicable